

Bulk and shear relaxation in glasses and highly viscous liquids

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The ratio $\delta B/\delta G$ between the couplings of a relaxational process to compression and shear, respectively, is calculated in the Eshelby picture of structural rearrangements within a surrounding elastic matrix, assuming a constant density of stable structures in distortion space. The result is compared to experimental data for the low-temperature tunneling states in glasses and to Prigogine-Defay data at the glass transition, both from the literature.

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I. INTRODUCTION

An amorphous solid reacts to an instantaneous affine shear deformation with the infinite frequency shear modulus G_∞ . But the atoms are not in equilibrium then; there is a non-affine motion of the atoms which lowers the energy^{1,2}, leading to a lower high-frequency modulus G . This motion is intimately related to the boson peak and to the tunneling states which dominate the glass behavior at very low temperatures^{3,4} as well as to the plastic modes responsible for the shear thinning in Non-Newtonian flow⁵. G is the shear modulus which one measures in a light-scattering Brillouin experiment at GHz frequency, a frequency markedly lower than the one of the boson peak.

In undercooled liquids, the flow process becomes so slow that one begins to see the shear modulus G for high enough frequencies^{6,7}. According to a very recent replica (or cloned liquid) theory result⁶, the point in temperature where one begins to see the shear modulus is the critical temperature of the mode coupling theory⁸, though numerical simulations⁹ see it already at a higher temperature.

If one begins to see a high frequency shear modulus, one also has to distinguish between the high-frequency and zero frequency bulk moduli B and B_0 , respectively (B_0 is the inverse of the isothermal compressibility). Though there is a standard textbook description of the viscoelastic liquid¹⁰, there is no theory relating $B - B_0$ to G . The mode coupling theory does not contain a shear modulus; in fact, if the new cloned liquid theory result⁶ is correct, the theory is no longer valid at the temperature where the shear modulus appears. The random first order theory (RFOT)¹¹ is supposed to be valid, but the RFOT specifies only the entropy and the surface tension of a rearranging region and thus does not supply the needed information. Similarly, the coupling model¹² does not specify a difference between compression and shear. The elastic models^{13,14} postulate a proportionality of the flow barrier to G (one wonders a bit whether they should not propose a proportionality to G_∞), but they make no selective prediction for compression or shear. The counting of covalent constraints^{15,16} allows one to count the number of floppy modes per atom in a given substance,

but tells nothing about a compression-shear ratio.

There are some specific atomic motion models, in particular for close-packed atoms interacting with a simple two-body potential, which do allow a prediction. One of them is the interstitial model¹⁷. In the crystal, the interstitial does not couple to an external compression, but only to an external shear¹⁸. Another one is the gliding triangle model¹⁹, which postulates a shear motion of two adjacent triangles of atoms with respect to each other. Both models predict the compression-shear ratio zero, because there is only a coupling to the shear. This result is indeed compatible with experiment and simulation in Lennard-Jones and metallic glasses²⁰, but not in other substances.

The only theoretical concept able to derive a prediction on general grounds is the Eshelby picture of local structural rearrangements within an elastic solid²¹⁻²⁴. The present paper derives a general relation for the compression-shear ratio on this basis.

The paper proceeds by the derivation of the general relation in Section II. Section III compares to experimental data from glasses and liquids. Section IV concludes and summarizes the paper.

II. THEORETICAL BASIS

A. Bulk and shear relaxation in the Eshelby picture

In the Eshelby scheme, one considers a strain-free ground state of a volume Nv_a of N atoms or molecules with an atomic or molecular volume v_a , embedded in an elastic matrix with the same elastic constants as the volume itself. A structural rearrangement to an alternative stable structure of the volume changes its shape. To first order, the shape change is a pure distortion, describable in terms of the inner volume change $u_i = \delta v_i/Nv_a$ and five linearly independent shear angles e_i (see Fig. 1).

After the rearrangement, both the inner and the outer volume end up in a strained state, because the alternative stable state has a misfit with respect to the matrix. The resulting elastic strain energy Δ is about half the energy

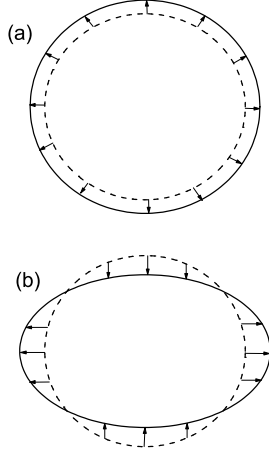


FIG. 1: The two types of Eshelby rearrangements (a) a pure volume change $u_i = \delta v_i/v$ (b) a pure shear e_i .

needed to squeeze the new stable state into the old hole without deforming it.

Let the initial volume be a sphere. According to Eshelby^{21,22}, for a specific pure volume change u_i

$$\Delta_b = \frac{2BG}{3B + 4G} N v_a u_i^2 = \frac{2}{9} \frac{1 + \nu}{1 - \nu} G N v_a u_i^2, \quad (1)$$

where the index b stands for a bulk distortion and ν is the Poisson ratio, related to the ratio B/G by

$$\frac{B}{G} = \frac{2(1 + \nu)}{3(1 - 2\nu)}. \quad (2)$$

The coupling constant γ_b to an external volume change $u = \delta v/v$ is given by

$$\gamma_b = -\frac{\partial \Delta_b}{\partial u_i} = -\frac{4}{9} \frac{1 + \nu}{1 - \nu} G N v_a u_i. \quad (3)$$

Similarly^{21,22}, for a pure shear change e_i

$$\Delta_s = \frac{7 - 5\nu}{30(1 - \nu)} G N v_a e_i^2, \quad (4)$$

where the index s stands for a shear distortion. The coupling constant γ_s to an external shear e in the direction e_i is

$$\gamma_s = -\frac{\partial \Delta_s}{\partial e_i} = -\frac{7 - 5\nu}{15(1 - \nu)} G N v_a e_i. \quad (5)$$

For equal asymmetries $\Delta_b = \Delta_s$ one has

$$\frac{\delta B}{\delta G} = \frac{\gamma_b^2}{\gamma_s^2} = \frac{20}{3} \frac{1 + \nu}{7 - 5\nu}. \quad (6)$$

In order to set the volume change on the same energy scale as the shear distortion, one defines the variable e_6 with

$$e_6^2 = \frac{20}{3} \frac{1 + \nu}{7 - 5\nu} u_i^2. \quad (7)$$

For the surface of the sphere $\Delta = \text{const}$ in the six-dimensional distortion space $e_1 \dots e_6$, one finds the maximum value for γ_b^2 along the e_6 -axis and the maximum value for γ_s^2 along any of the five shear axes. These maximum values have again the ratio of eq. (6). For a constant density of stable states in distortion space, the average values are just 1/6 of these maximum values. Therefore eq. (6) should also hold for the average values on the sphere surface. Integrating over Δ , one then gets the relation for the whole ensemble.

B. The thermodynamics of the glass transition

At the glass transition, $\delta B/\delta G$ cannot be directly determined from $(B - B_0)/G$, because one has to take the enthalpy-volume correlation into account^{20,25}. At T_g , one has to distinguish the density fluctuations which are correlated with the enthalpy from those which are not. Even a pure shear rearrangement which increases the structural energy increases the volume because of the anharmonicity of the interatomic potential. This second kind of density fluctuations is intimately related to the additional thermal expansion of the undercooled liquid.

A quantitative thermodynamic treatment of the additional thermal expansion has been given in the parallel paper²⁰. According to this treatment, one can determine the coupling constant ratio $\delta B/\delta G$ from the measurements at T_g via

$$\frac{\delta B}{\delta G} = \frac{B \Delta \kappa (\Pi - 1)}{1 + B \Delta \kappa (\Pi - 1)} \frac{B}{G}, \quad (8)$$

where Π is the Prigogine-Defay ratio of the glass transition²⁶

$$\Pi = \frac{\Delta c_p \Delta \kappa}{(\Delta \alpha)^2 T_g} = \frac{\overline{\Delta H^2} \overline{\Delta V^2}}{(\overline{\Delta H \Delta V})^2}, \quad (9)$$

which relates the increases of the heat capacity at constant pressure per volume unit Δc_p , of the compressibility $\Delta \kappa$ and of the thermal volume expansion $\Delta \alpha$ at the glass temperature T_g to the additional enthalpy and volume fluctuations ΔH and ΔV , respectively. If the enthalpy and volume fluctuations are completely correlated, the Prigogine-Defay ratio is one. Eq. (8) shows that this is equivalent to $\delta B/\delta G = 0$.

III. COMPARISON TO EXPERIMENTS IN GLASSES AND LIQUIDS

The theoretical curve of eq. (6) is shown as a continuous line in Fig. 2. Also shown are experimental data from the literature: the full circles are $30 \gamma_b^2/\gamma_s^2$ -values determined for tunneling states in 26 glasses at low temperatures²⁹⁻³¹, the open symbols are measurements of $\Delta B/G = (B - B_0)/G$ in undercooled liquids from Tables I and II.

subst.	\bar{M}	T_g	ρ	α_g	α_l	B	B_0	c_{pg}	c_{pl}	ν	Π	$\delta B/\delta G$	
	a. u.	K	kg/m ³	10 ⁻⁴ K ⁻¹		GPa		10 ⁶ J/m ³				at T _g	tunn.
a) silicates:													
SiO ₂	20.00	1480	2198	.017	.009	45.05	12.66	2.68	2.98	.18	>100	1.23	1.2 ^a
15.4 % Na ₂ O	20.10	773	2314	.23	.55	36.10	15.87	2.66	3.01	.24	15.19	1.53	
20.5 % Na ₂ O	20.14	746	2352	.32	.74	35.09	17.06	2.74	3.20	.27	10.66	1.68	
25 % Na ₂ O	20.17	736	2380	.40	.95	35.21	16.67	2.81	3.36	.29	7.62	1.80	
25.5 % Na ₂ O	20.17	734	2392	.40	.97	35.21	18.52	2.82	3.37	.29	5.90	1.69	
26.6 % Na ₂ O	20.18	733	2403	.42	1.02	35.21	18.52	2.84	3.42	.30	5.70	1.72	
29.7 % Na ₂ O	20.20	725	2415	.47	1.19	34.97	19.31	2.87	3.53	.31	4.03	1.63	
33.4 % Na ₂ O	20.22	715	2433	.53	1.42	35.09	20.51	2.92	3.65	.33	2.61	1.36	
39.6 % Na ₂ O	20.26	683	2457	.63	1.83	34.97	21.01	2.97	3.81	.35	1.61	.89	
43.0 % Na ₂ O	20.28	671	2463	.69	2.06	35.09	20.62	3.01	3.89	.37	1.40	.76	
49.5 % Na ₂ O	20.33	648	2475	.78	2.56	35.21	20.12	3.07	4.03	.40	1.00	.01	
12.4 % K ₂ O	21.40	795	2293	.23	.64	32.57	14.10	2.50	2.94	.23	12.93	1.45	
19.5 % K ₂ O	22.22	763	2347	.33	.95	30.67	15.31	2.42	2.93	.27	5.75	1.49	
23.6 % K ₂ O	22.69	748	2375	.39	1.11	29.76	14.84	2.38	2.97	.28	5.18	1.60	
28.4 % K ₂ O	23.24	729	2398	.46	1.30	29.15	14.97	2.40	3.00	.31	3.75	1.61	
33.9 % K ₂ O	23.86	713	2421	.53	1.52	28.90	16.21	2.42	3.03	.33	2.35	1.33	
39.0 % K ₂ O	24.45	683	2427	.59	1.74	27.86	17.48	2.39	3.01	.35	1.47	.66	
b) borates:													
B ₂ O ₃	13.92	550	1792	.54	4.00	10.00	2.56	2.37	3.44	.28	4.71	1.77	1.66 ^b
6.2 % Na ₂ O	14.34	605	1949	.31	3.92	19.61	2.93	2.77	4.00	.29	4.52	1.93	
9.3 % Na ₂ O	14.55	643	2000	.28	3.35	22.27	3.95	2.96	4.18	.29	4.19	1.94	
11.1 % Na ₂ O	14.67	663	2040	.27	3.05	25.51	4.55	3.07	4.35	.29	4.49	1.97	
14.1 % Na ₂ O	14.87	707	2079	.26	2.45	27.25	5.41	3.22	4.43	.30	5.29	2.03	
15.7 % Na ₂ O	14.98	726	2105	.26	2.30	27.55	5.99	3.26	4.48	.30	5.31	2.05	
17.5 % Na ₂ O	15.10	731	2132	.27	2.15	27.70	6.69	3.26	4.54	.30	5.62	2.06	
19.2 % Na ₂ O	15.20	736	2155	.28	2.10	29.41	7.57	3.25	4.59	.31	5.38	2.07	
21.4 % Na ₂ O	15.36	741	2188	.28	2.07	31.85	8.36	3.19	4.57	.31	5.12	2.09	
24.6 % Na ₂ O	15.57	743	2227	.31	2.26	35.97	10.78	3.16	4.57	.31	3.24	1.95	
29.8 % Na ₂ O	15.93	743	2304	.38	3.00	40.00	10.60	3.36	4.86	.32	2.04	1.80	
35.0 % Na ₂ O	16.28	723	2325	.41	3.82	40.82	9.42	3.07	4.91	.33	1.79	1.84	
4 % K ₂ O	14.34	597	1923	.46	4.05	18.87	2.42	2.81	3.98	.28	5.49	1.92	
5 % K ₂ O	14.44	603	1937	.45	3.95	19.61	2.75	2.87	4.05	.28	5.00	1.91	
8 % K ₂ O	14.76	627	1988	.40	3.45	15.55	3.56	3.24	4.37	.29	4.21	1.84	
10 % K ₂ O	14.96	643	2016	.38	3.15	22.68	4.74	3.21	4.52	.29	4.43	1.89	
15.5 % K ₂ O	15.54	677	2066	.35	2.35	25.06	6.01	3.37	4.67	.29	6.08	1.97	
19.5 % K ₂ O	15.96	697	2092	.35	2.10	25.97	6.85	3.33	4.54	.30	6.11	2.00	
20 % K ₂ O	16.02	698	2096	.35	2.10	25.97	7.20	3.33	4.55	.30	5.71	1.99	
30 % K ₂ O	17.07	725	2212	.45	3.00	28.82	8.35	2.88	3.89	.31	1.84	1.53	

TABLE I: Coupling ratio $\delta B/\delta G$ from Prigogine-Defay data and Poisson ratios for silicates and borates at the glass transition. Prigogine-Defay data (average atomic mass \bar{M} , glass temperature T_g , density ρ , glass and liquid thermal volume expansion coefficients α_g and α_l , glass and liquid bulk moduli B and B_0 , glass and liquid heat capacities per unit volume at constant pressure c_{pg} and c_{pl}) taken from reference³². The Poisson ratio for silica is from Bucaro and Dardy³³, the one for 33% Na₂O from Webb³⁴. For the other silicates, the Poisson ratios were interpolated assuming a linear dependence on concentration with equal coefficients for Na₂O and K₂O. The Poisson ratio for the borates taken (again assuming a linear concentration dependence) from reference³⁵. Tunneling data ^aBerret and Meissner²⁹; ^bPohl et al³⁰.

The experimental values for the tunneling states were taken from the data collections of Berret and Meissner²⁹, Pohl, Liu and Thompson³⁰ and Bellessa³¹. Berret and Meissner report values for the tunneling state coupling constants γ_l and γ_t to longitudinal and transverse sound waves, respectively. γ_t agrees with the γ_s of the present paper. For γ_l , one has the relation

$$\gamma_l^2 = \gamma_b^2 + \frac{4}{3}\gamma_s^2, \quad (10)$$

because the longitudinal modulus $M = B + 4G/3$. Thus one can calculate $\delta B/\delta G = \gamma_b^2/\gamma_s^2$ from γ_l and γ_t . Pohl,

Liu and Thompson³⁰ report values of C_l and C_t from tunneling plateaus in the damping of longitudinal and transverse waves at low temperatures in glasses. From these and the sound velocities v_l and v_t , one can again calculate γ_l^2/γ_t^2 via

$$\frac{\gamma_l^2}{\gamma_t^2} = \frac{C_l v_l^2}{C_t v_t^2}. \quad (11)$$

Bellessa³¹ reports values of $n_0\gamma_l^2$ and $n_0\gamma_t^2$ from the temperature dependence of the sound velocities at low temperature in selenium and in three metallic glasses, where

subst.	\bar{M}	T_g	ρ	α_g	α_l	B	B_0	c_{pg}	c_{pl}	ν	Π	$\delta B/\delta G$	
	a. u.	K	kg/m ³	10 ⁻⁴ K ⁻¹		GPa		10 ⁶ J/m ³				at T_g	tunn.
a) molecules:													
glycerol	6.57	183	1316	.90	4.80	11.10	5.56	1.30	2.46	.36	3.73	2.37	
glucose	7.50	282	1540	.90	2.60	10.75	6.49	.81	1.30	.38	3.71	2.45	
DC704	7.40	214	1080	1.40	4.60	5.26	3.54	1.35	1.65	.40	1.26	.54	
o-terphenyl _{0.67} o-phenylphenol _{0.33}	7.25	236	970	1.69	7.37	5.26	2.93	1.16	1.76	.36	1.19	.43	
b) polymers:													
polyisobutylene	4.66	198	952	1.50	6.20	3.33	2.50	1.20	1.62	.39	.96	-.06	
polyvinylacetate	7.16	304	1190	2.80	7.10	3.45	2.00	1.55	2.14	.31	2.22	1.08	
polyvinylchloride	10.41	350	1370	2.00	5.70	4.17	2.27	1.59	2.00	.36	1.72	1.25	
polystyrene	6.50	362	1031	2.30	5.73	3.12	1.64	1.55	1.80	.36	1.70	1.22	
polymethylmethacrylate	6.66	378	1149	2.57	6.06	3.33	1.72	1.75	2.10	.32	2.14	1.26	1.27 ^a
bisphenol-A-polycarbonate	6.91	423	1159	2.55	5.99	2.93	1.88	1.45	1.72	.39	1.03	.06	0.11 ^b
c) others:													
GeO ₂	34.86	933	3590	.27	.76	23.87	8.08	2.42	2.61	.16	6.85	1.05	0.9 ^b
Ca ₂ K ₃ (NO ₃) ₇	19.14	340	2174	1.20	3.50	16.66	7.69	2.07	3.24	.36	4.57	2.61	
selenium	78.96	304	4167	1.70	4.20	4.16	3.33	1.38	2.13	.34	2.37	.71	0.8 ^c
anorthite	21.39	1093	2699	.19	.52	40.50	20.60	3.02	3.97	.27	19.04	1.73	
diopside	21.70	993	2861	.35	1.25	32.20	24.10	3.05	4.67	.28	2.10	0.53	

TABLE II: Coupling ratio $\delta B/\delta G$ from Prigogine-Defay data and Poisson ratios for molecules, polymers and other glass formers at the glass transition. DC704 is a diffusion pump oil, tetramethyl-tetraphenyl-trisiloxane. References for Prigogine-Defay data: anorthite and diopside Dingwell et al³⁶ and Schilling et al³⁷; polymethylmethacrylate Sane and Knauss³⁸, Krüger et al³⁹, Bares and Wunderlich⁴⁰ and Schwarzl⁴¹; all other substances from the supplement of Gundermann et al²⁵. References for Poisson ratios (or for the shear modulus G , because B is known from the Prigogine-Defay data): glycerol Fioretto et al⁴²; glucose Meyer and Ferry⁴³; DC704 Niss et al⁴⁴; o-terphenyl_{0.67}o-phenylphenol_{0.33} assumed to be the one of OTP from Tölle et al⁴⁵; polyisobutylene Litovitz and Davis⁴⁶; polyvinylacetate Donth et al⁴⁷; polyvinylchloride Kono⁴⁸; polystyrene Takagi et al⁴⁹; polymethylmethacrylate Krüger et al³⁹; bisphenol-A-polycarbonate Patterson⁵⁰; GeO₂ Ananьев et al⁵¹; Ca₂K₃(NO₃)₇ Torell and Aronsson⁵²; selenium Soga et al⁵³; anorthite and diopside Schilling et al³⁷. Tunneling data ^aBerret and Meissner²⁹; ^bPohl et al³⁰; ^cBellessa³¹.

n_0 is the density of tunneling states. From the ratio of these two values, one can again calculate $\delta B/\delta G$ as from the data of Berret and Meissner.

The error is large; if γ_l^2 and γ_t^2 are measured with an error of 10 %, the error of $\delta B/\delta G$ is 40 %. But the scatter of the data is even larger than the one expected from the error. This is a first indication for a large substance

dependence of $\delta B/\delta G$.

Table I and Table II compile literature data for the Prigogine-Defay ratio and the Poisson ratio. With these, one can calculate $\delta B/\delta G$ from eq. (8). The results in Fig. 2 show a similar scatter and a similar dependence on the Poisson ratio as those determined from the tunneling states at low temperatures. Not only the glass transition data, but also the tunneling state coupling constants follow the theoretical curve of eq. (6) at small Poisson ratio ν . At about $\nu = 1/3$, the value for central forces in close packing, the values begin to decline away from the theoretical curve, reaching zero at about $\nu = 0.4$.

The equality of the coupling ratios at the glass transition and for the low temperature tunneling states is the first main result of the present paper. Note that the few substances in Table I and II where both couplings have been measured show agreement within experimental error.

The second main result is the gradual breakdown of the theoretical prediction as the Poisson ratio begins to approach higher values. Obviously, the assumption of a constant density of stable structural states in distortion space, on which the theoretical prediction is based, breaks down as the Poisson ratio of the glass approaches the value 1/2 of the liquid. The reason for this breakdown is not yet clear, but it tends to occur in close-packed systems²⁰.

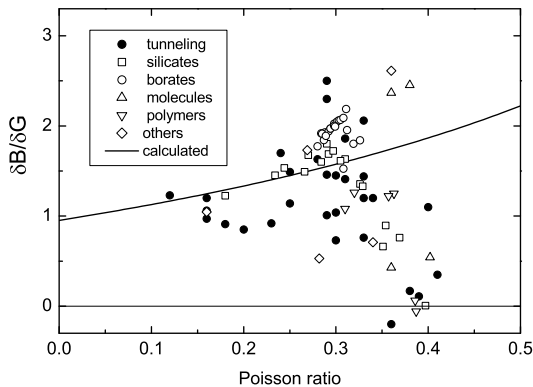


FIG. 2: Ratio $\delta B/\delta G$ as a function of the Poisson ratio. The continuous line is the Eshelby prediction of eq. (8). The full circles are experimental data for tunneling states in glasses^{29–31}, the open symbols glass transition values from Tables I and II.

IV. SUMMARY

The Eshelby concept of a local structural rearrangement within a surrounding elastic matrix allows to derive the coupling ratio $\delta B/\delta G$ of structural relaxation processes to an external compression and an external shear, respectively. Assuming a constant density of stable structures in distortion space, one finds a ratio between one and two, increasing with increasing Poisson ratio.

The comparison to literature data from the low temperature tunneling states in glasses provides essentially the same answer as the comparison to literature glass

transition data: At low Poisson ratio, the theoretical prediction is obeyed, though with a large scatter from a strong substance dependence of the ratio. Above the Poisson ratio 1/3, the coupling ratio decreases, reaching zero at a Poisson ratio of about 0.4. At this point, the Prigogine-Defay ratio of the glass transition reaches unity, implying a perfect correlation of the additional enthalpy and the density fluctuations which distinguish the liquid from the glass.

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